Review

Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems, and solutions

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ABSTRACT

Lithium/sulfur (Li/S) battery has a 3—5 fold higher theoretical energy density than state-of-art lithium-ion batteries, and research has been ongoing for more than three decades. However, the commercialization of Li/S battery still cannot be realized due to many problematic issues, including short cycle life, low cycling efficiency, poor safety and a high self-discharge rate. All these issues are related to the dissolution of lithium polysulfide (PS), the series of sulfur reduction intermediates, in liquid electrolyte and to resulting parasitic reactions with the lithium anode and electrolyte components. On the other hand, the dissolution of PS is essential for the performance of a Li/S cell. Without dissolution of PS, the Li/S cell cannot operate progressively due to the non-conductive nature of elemental sulfur and its reduction products. In this review article, we start with the fundamental chemistry of elemental sulfur in order to discuss the problems and solutions of liquid electrolyte Li/S battery.

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1. Introduction

With the energy density of the Li-ion battery approaching its ceiling, researchers have recently moved their interest to systems beyond Li-ion. Due to the abundance and low cost of elemental sulfur, lithium/sulfur (Li/S) battery has been considered to be a preferential choice. According to the complete reduction from elemental sulfur to lithium sulfide (Li_2S), sulfur is expected to deliver a specific capacity of 1675 Ah Kg^{-1} and an energy density of 2600 Wh Kg^{-1}, which are 3—5 folds higher than those of state-of-art Li-ion batteries. Although the study on this subject has been ongoing over three decades, commercialization of the Li/S battery has not been successful due to many problematic issues. The known problems include short cycle life, low charging efficiency, poor

safety, and a high self-discharge rate. All these problems are related to the dissolution of lithium polysulfide (PS, Li_2S_n), the series of sulfur reduction intermediates, in liquid electrolyte and resulting parasitic reactions. On the other hand, the dissolution of PS is essential for the performance of a Li/S cell. Since both elemental sulfur and its reduction products are non-conductive, the reduction of sulfur and PS only can take place on the surfaces of conductive carbon. By dissolution, the soluble PS dissolves into electrolyte solution, which leaves remaining sulfur exposed to the conductive carbon so that the reduction can progressively move forward. Most of the recent efforts have been focused on the reduction of the adverse effects caused by the dissolution of PS, which includes either suppressing diffusion of the dissolved PS out of the cathode or protecting lithium anode from reacting with the dissolved PS. In this review article, we will start with the fundamental chemistry of elemental sulfur in order to discuss the problems and solutions of Li/S batteries.

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2. Fundamental chemistry of Li/S cell

2.1. Basic property of sulfur

Sulfur is the seventeenth richest element in the Earth's crust, and it has over 30 solid allotropes. In nature, the most common form is cyclic octasulfur (S_8), followed by the cyclic S_{12} allotrope [1]. Octasulfur has three forms of α-sulfur, β-sulfur, and γ-sulfur, of which the β-sulfur and γ-sulfur are metastable, they convert to α-sulfur in storage at ambient temperature. The α-sulfur melts at 115.21 °C, boils at 444.6 °C, and sublimes easily. In the molten state, sulfur exhibits a unique viscosity—temperature behavior. On heating, the viscosity of the sulfur melt slowly decreases, followed by a remarkable increase around 160 °C as a result of the opening and polymerization of the S_8 rings until near 190 °C at which sulfur starts depolymerizing and the viscosity decreases [2,3]. Therefore, there is a minimum viscosity value near 160 °C. This feature has been widely adopted to impregnate sulfur into porous materials for the preparation of sulfur composite materials.

Allotropes with rings of 9-5, 18 and 20 sulfur atoms are formed above 160 °C, and quenching of this melt forms amorphous sulfur, which is elastic and metastable. Upon storage, the amorphous sulfur reverts to a crystalline allotrope. The allotropes with 2—5 sulfur atoms are only present in vapor above 720 °C or slightly lower temperatures under lower pressure [3,4]. These small molecular sulfur allotropes revert to the solid allotrope (S_8) once the temperature cools down.

Sulfur is slightly soluble in many polar electrolyte solvents [5]. Unlike elemental sulfur, small polysulfide anions (S_n^{2-} with $n = 2-5$) can be formed readily and stably in solution. For example, the PS solution (Li_2S_n with $n > 2$) can be easily prepared through the reaction of elemental sulfur and lithium sulfide (Li_2S) [6]. As Table 1 shows [7], The Gibbs free-energy (ΔG^o) of each polysulfide anion is so close that these anions are co-existent in the solution through a series of chemical equilibriums.

2.2. Voltage characteristic of Li/S cell

Fig. 1 shows a typical discharge and charge voltage profile for the first cycle of Li/S cells. Based on the phase change of sulfur species, the discharge process can be divided into four reduction regions:

Region I: A solid—liquid two-phase reduction from elemental sulfur to Li_2S_8, which shows the first upper voltage plateau at 2.2—2.3 V. In this region, the formed Li_2S_8 dissolves into liquid electrolyte to become a liquid cathode. This process leaves numerous voids in the cathode.

$$S_8 + 2Li \rightarrow Li_2S_8 \quad (1)$$

Region II: A liquid—liquid single-phase reduction from the dissolved Li_2S_8 to low-order PS, during which the cell's voltage steeply declines and the solution's viscosity gradually increases with a decrease in the length of S—S chain and an increase in the number (concentration) of PS anions. The solution's viscosity reaches a maximum value in the end of the discharge region.

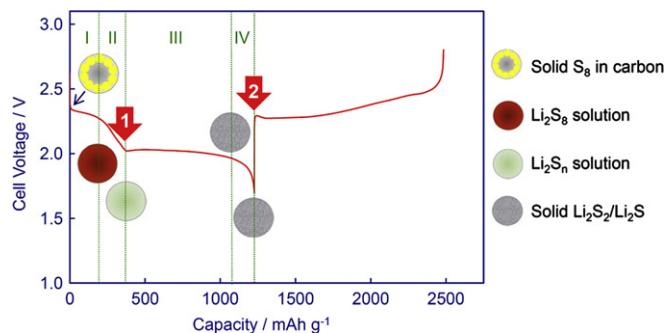$$Li_2S_8 + 2Li \rightarrow Li_2S_{8-n} + Li_2S_n \quad (2)$$

Fig. 1. A typical discharge and charge voltage profile of the first cycle of Li/S cells.

Region III: A liquid—solid two-phase reduction from the dissolved low-order PS to insoluble Li_2S_2 or Li_2S, during which Eqs. (3) and (4) are competing with each other. This region forms the second lower voltage plateau at 1.9—2.1 V, which contributes to the major capacity of a Li/S cell.

$$2Li_2S_n + (2n-4)Li \rightarrow nLi_2S_2 \quad (3)$$

$$Li_2S_n + (2n-2)Li \rightarrow nLi_2S \quad (4)$$

Region IV: A solid—solid reduction from insoluble Li_2S_2 to Li_2S. This process is kinetically slow and generally suffers from high polarization due to the non-conductive and insoluble natures of Li_2S_2 and Li_2S.

$$Li_2S_2 + 2Li \rightarrow 2Li_2S \quad (5)$$

Among four regions above, Regions I and II show the highest redox shuttle, during which the cell suffers from the highest self-discharge rate and the cell's theoretical capacity can be seldom obtained. Region III contributes to the major capacity of a Li/S cell. When Eq. (4) is predominant, the cell gives high capacity, and accordingly Region IV becomes very short or even vanishes. Beside the electrochemical reductions, the complicated chemical reactions between PS anions are also present in the electrolyte solution, which are affected by the solvents, concentration and temperature of PS solution. These reactions can be generally described by Eqs. (6) and (7) [8]:

$$Li_2S_n + Li_2S \rightarrow Li_2S_{n-m} + Li_2S_{1+m} \quad (6)$$

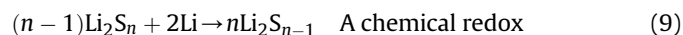$$Li_2S_n \rightarrow Li_2S_{n-1} + 1/8S_8 \quad (7)$$
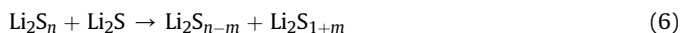
Typically, the voltage of discharge and charge, respectively, shows a small peak, as indicated by two arrows in Fig. 1. Arrow 1 corresponds to a point at which the PS solution has the highest viscosity as a combined result of the S—S chain length and number (concentration) of PS anions. Arrow 2 reflects a reduced polarization as a result of the phase transition from the solid Li_2S_2 and Li_2S to the dissolved PS. At the discharged state, the surfaces of carbon are covered by a solid Li_2S_2/Li_2S layer so that the cell suffers from high polarization. Upon charge, the solid Li_2S_2 and Li_2S are oxidized

Table 1
Thermodynamic data of various PS anions (S_n^{2-}) formed in aqueous solution [7].

S_n^{2-} with	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
ΔG^o, kJ mol^{-1}	77.4 ± 1.3	71.1 ± 0.7	67.1 ± 0.1	66.0 ± 0.1	67.4 ± 0.1	70.7 ± 0.3	74.9 ± 0.5
ΔH^o, kJ mol^{-1}	13.0	6.6 ± 0.1	9.0 ± 0.1	9.6 ± 0.1	13.3 ± 0.1	16.5 ± 0.1	23.8 ± 0.2
S^o, kJ mol^{-1} K^{-1}	−22	9 ± 4	63 ± 1	100 ± 2	139 ± 1	171 ± 4	213 ± 8

into the soluble PS which dissolves into the liquid electrolyte, resulting in a reduction in the cell's polarization.

Based on the analyses above, the Li/S cell is really a liquid electrochemical system. In Region I, sulfur is entirely dissolved into the liquid electrolyte in the form of Li_2S_8, further reduction of the dissolved PS takes place on the surfaces of carbon. Therefore, the initial mixing status of sulfur and carbon in the cathode is not important for the performance of a Li/S cell [9]. This concept has been well verified by a Li/S cell consisting of a dual-layer structural sulfur cathode as shown in Fig. 2. In such a cell, the cathode having a sulfur loading of over 10 mg cm^{-2} is composed of a porous carbon cloth as the current collector and a porous sulfur paper as the sulfur source [10]. Since both sulfur and its reduction products are non-conductive, the operation of such a cell entirely depends on the dissolution of PS. The reasonable specific capacity ($\sim$800 mAh g^{-1} in the first cycle remained at 510 mAh g^{-1} after 60 cycles when being cycled at 1.27 mA cm^{-2} between 1.7 V and 2.8 V) of this cell reveals the important role of the PS dissolution in determining the cycling performance of a Li/S cell.

2.3. Redox shuttle of PS

While facilitating cell's performance, the dissolved PS causes severe redox shuttle between the sulfur cathode and Li anode, which results in a low coulombic efficiency for charging and a fast self-discharge rate for storage. On Li anode, the dissolved PS can be electrochemically and chemically reduced, as described by Eqs. (8) and (9), respectively:

$$(n-1)Li_2S_n + 2Li^+ \\ + 2e^- \rightarrow nLi_2S_{n-1} \quad \text{An electrochemical reduction} \tag{8}$$

$$(n-1)Li_2S_n + 2Li \rightarrow nLi_2S_{n-1} \quad \text{A chemical redox} \tag{9}$$

These parasitic reactions cause such problems as (1) consuming active sulfur species, (2) corroding Li anode, and (3) polarizing Li anode once the insoluble Li_2S and Li_2S_2 are formed and deposited on the Li surface. The effect of PS redox shuttle is clearly reflected in the cell's charging and discharging voltage, as indicated in Fig. 3, where Cell 1 suffers from a strong redox shuttle while Cell 2 has a good redox shuttle suppression by using a $LiNO_3$-containing electrolyte [11]. It is shown that Cell 1 cannot be charged above 2.5 V and the charging process has to be terminated by a pre-set charging capacity. In this case, the cell only can be charged to the end of Region I without the formation of elemental sulfur due to the strong redox shuttle of the dissolved Li_2S_8. In contrast, Cell 2 can be easily charged to the pre-set cutoff voltage with the formation of elemental sulfur and the subsequent discharge displays a distinct upper voltage plateau at $\sim$2.3 V, leading to a cycling efficiency of over 99%.
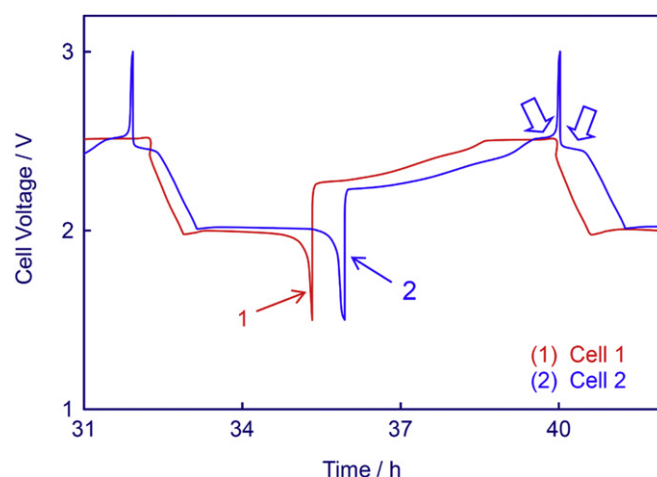
Fig. 3. Charge and discharge voltage curves of Li/S cells, in which Cell 1 shows strong redox shuttle and Cell 2 has redox shuttle well-suppressed. Reproduced from Ref. [11] with permission of Elsevier.

3. Problems and requirements for Li/S cell's materials

3.1. Sulfur cathode

Sulfur and its reduction products are non-conductive and they have a relatively low gravity density (2.07 g cm^{-3} for α-sulfur and 1.66 g cm^{-3} for Li_2S). In most cases, a large amount of conductive carbon should been mixed with sulfur to obtain the necessary electronic conductivity for the cell's operation. To retain the advantage of sulfur's high energy density, the cathode is required to have a sulfur content of at least 70% by weight and a reasonable sulfur loading of equaling to a specific capacity of 2−3 mAh cm^{-2}.

3.1.1. Conducting agent

Reduction from elemental sulfur to Li_2S leads to a volumetric increase by 79.2%. Therefore, high porosity is required for the conductive carbon to accommodate the increased volume. While high content of the conductive carbon favors increasing the specific capacity and capacity retention of sulfur, it reduces the cell's energy density. In many cases, functional groups on the carbon surface are helpful for increasing the chemical adsorption of PS anions from the PS solution.

3.1.2. Binder

In the end of discharge Region I, all sulfur species are dissolved into liquid electrolyte, which leaves numerous voids in the cathode, whereas in Regions III, the dissolved PS deposit back onto the cathode in the forms of Li_2S_2 and Li_2S. This requires the binder capable of retaining the very highly porous structure of the cathode in the cycling process of a Li/S cell. The conventional binders such as poly(vinylidene fluoride) (PVDF) and poly(ethylene oxide) (PEO) cannot meet this requirement because of the swelling or gelling by the electrolyte solvents. In addition, sulfur reduction produces anionic polysulfide radicals (S_n^-) as the intermediate, which react with many organic polymers. For example, simply ball-milling a slurry consisting of sulfur and poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) in acetonitrile solvent leads to a strong odor of thiols, which suggests a possible reaction between the elemental sulfur and PVDF−HFP molecules [12]. Sulfur and PS react with polymers containing unsaturated >C=C< bonds such as natural and synthetic rubbers, i.e., so-called "vulcanization". Therefore, a qualified binder for the cathode of a Li/S cell should be inswellable in the liquid electrolyte and chemically stable against all types of sulfur species.
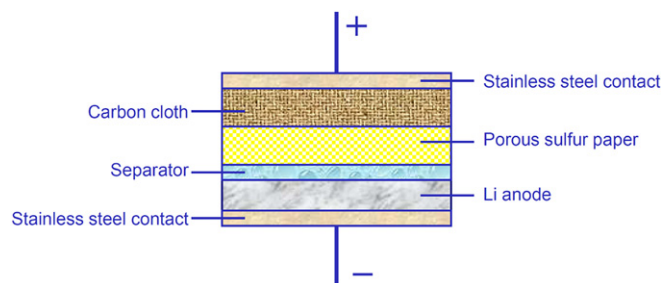
Fig. 2. Schematic configuration of a Li/S cell with a dual-layer structural sulfur cathode. Reproduced from Ref. [10] with permission of Elsevier.

3.1.3. Current collector

Aluminum (Al) foil has been widely used as the current collector of sulfur cathode. This could result in a safety issue since at high temperature, Al metal and sulfur can react violently with each other. Carbon-coated Al foil can avoid the direct contact of Al metal and sulfur, which increases the safety of a Li/S cell. Furthermore, the carbon-coating layer enhances the adhesion of the cathode components to the current collecting substrate.
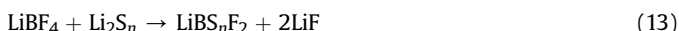
3.2. Electrolyte

3.2.1. Solvent

PS anions and anionic PS radicals are extremely reactive, they participate in many types of reactions such as basic, nucleophilic, redox, and radical reactions. PS is known to react with most of the common electrolyte solvents, such as esters, carbonates, and phosphates [13]. It appears that the suitable solvents for the Li/S cell electrolytes are only limited within the linear and cyclic ethers, such as dimethyl ether (DME) and 1,3-dioxolane (DOL). Overall, the linear DME offers higher PS solubility and faster PS reaction kinetics while being more reactive with Li metal, whereas the cyclic DOL forms more stable solid electrolyte interface on the Li surface while providing lower PS solubility and slower PS reaction kinetics. Therefore, the combination of DME and DOL leads to synergetic effects on the specific capacity and capacity retention of sulfur as compared with the solvent alone [14]. Even thus, the solvents are still gradually depleted with cycling of the Li/S cells due to the reactions of solvent molecules with PS and Li metal, such as Eqs. (10) and (11), which results in the cell performance fading and gassing (swelling).

$$R-O-R + Li_2S_n \rightarrow R-OLi + R-S_nLi \tag{10}$$

$$R-O-R + 2Li \rightarrow 2R-OLi + R-R + \dots \tag{11}$$

Although the dissolution of PS causes parasitic redox shuttle reactions, the solvents with high PS solubility and low viscosity are greatly favorable for the cycling performance of a Li/S cell. Without PS's dissolution, the reduction of elemental sulfur only can occur on the sulfur—carbon interface, the bulk sulfur cannot be utilized, resulting in very low specific capacity. Even in the sulfur—carbon composites containing a significant amount of carbon, the dissolution of PS in the liquid electrolyte still is highly desired with the only difference being that the dissolved PS are physically trapped on the surfaces or/and in the pores of carbon. Therefore, the ideal solvent should meet the following criteria: (1) it is chemically stable against PS species (anions and anionic radicals) and Li anode, (2) it offers high PS solubility, and (3) it has low viscosity for PS solution.

3.2.2. Lithium salt

Chemical compatibility with PS is the highest priority for the selection of lithium salts. The conventional lithium salts such as LiPF$_6$, LiBF$_4$, lithium bisoxalatoborate (LiBOB) and lithium difluoro(oxalato)borate (LiBF$_2$C$_2$O$_4$) are not suitable for the electrolyte of Li/S cells because of the reactions, such as:

$$LiPF_6 + Li_2S_n \rightarrow LiPS_nF_4 + 2LiF \tag{12}$$

$$LiBF_4 + Li_2S_n \rightarrow LiBS_nF_2 + 2LiF \tag{13}$$

And the like reactions.

In addition, these salts cannot be used along with DOL, one of the most common co-solvents for the Li/S cell electrolytes, due to their Lewis acid property that initiates DOL molecules ring-opening polymerization. Special caution should be given to the use of LiClO$_4$

and LiNO$_3$ because of their oxidative property although no safety issue has been reported yet. So far, LiSO$_3$CF$_3$ and LiN(SO$_2$CF$_3$)$_2$ have been reported to be the most suitable salt for the electrolyte of Li/S cells, of which LiN(SO$_2$CF$_3$)$_2$ is superior in providing higher ionic conductivity and less corrosion to the Al substrate [15]. However, the LiN(SO$_2$CF$_3$)$_2$ solutions have higher viscosity as compared with those composed of LiSO$_3$CF$_3$.

3.3. Lithium anode

In the Li/S cells, dendrite deposition of Li metal is not as severe as those observed in other lithium cell systems. This is attributed to the dissolved PS, which prevents the growth of Li dendrites. As Eq. (9) suggests, the dendrite Li preferentially reacts with the dissolved PS due to its high specific surface area, which chemically "dissolves" the Li dendrites. The main problem of the Li anode is the low coulombic efficiency and rough/loose morphology of Li plating [14], both of which are associated with the PS redox shuttle. Rough and loose Li has a very large specific surface area, and is highly reactive with the electrolyte solvents. The reactions of Li and electrolyte solvents lead to gaseous and solid products, which is one of the most important causes for the capacity fading of Li/S cells. In addition, the reactions between Li metal and the dissolved PS have been identified to be the most important factor in initializing the thermal runway of the Li/S cells at high temperatures.

4. Solutions to the problems

As stated above, most of the Li/S cell's problems are attributed to the dissolution of PS and resulting parasitic reactions. Redox shuttle only occurs during the charging process, which results in low coulombic efficiency and worsens the Li morphology. Whereas the parasitic reactions of PS with electrolyte solvents and Li anode accompany the whole life of the cell, which affects the cell's capacity retention, self-discharge rate, and safety. Since dissolution of PS in the liquid electrolyte is inevitable and is essential for the cell's performance, previous efforts were mainly focused on the suppression of the diffusion of dissolved PS out of the cathode and on the protection of Li anode from reactions with PS. These approaches can be summarized as follows.

### 4.1. Trapping of the dissolved PS within cathode

Based on the physical adsorption and absorption, numerous porous materials have been attempted to trap the dissolved PS from diffusion out of the cathode. According to the type of adsorbents, these materials are classified as follows.

4.1.1. Porous carbon

A variety of porous carbon materials have been employed to make a so-called "sulfur—carbon composite" for the improvement of Li/S cell's performance. The advantage of carbon materials is their highly electronic conductivity. In addition to trapping PS species, the conductive carbon also provides sites for the reactions of sulfur and PS. According to the structure of pores, the carbon materials can be categorized as amorphous carbon (carbon black) [16–18], macro-, meso-, micro-porous carbon [19–23], carbon nanofibers [24,25], carbon nanotubes [26–30], carbon spheres [31,32], as well as various types of graphite such as expanded graphite [33], graphene [34–36], graphene oxide [37], and reduced graphene oxide [38].

Sulfur—carbon composites are generally prepared by a melt method or by a solution method. The melt method adopts the feature that the molten sulfur has the lowest viscosity near 160 °C to

impregnate sulfur into the pores of carbon [19,20]. The solution method is to dissolve sulfur into a solvent such as carbon disulfide (CS_2), toluene, or dimethyl sulfoxide (DMSO), followed by adding porous carbon into the solution to absorb the dissolved sulfur [17,18]. These two methods may result in different allotropes of sulfur, however, they do not affect the performance of the sulfur−carbon composites since all allotropes eventually convert into α-sulfur at room temperature and dissolve into the liquid electrolyte in the form of Li_2S_8 in the first discharge. In addition, the sulfur−carbon composite was also reported to be prepared by the in-situ decomposition method of thiosulfate through the following reaction [39,40]:

$$S_2O_3{}^{2-} + 2H^+ \rightarrow S + SO_2 + H_2O \qquad (14)$$
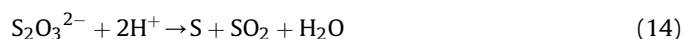
An interesting work was presented by Jayaprakash et al. [32] who synthesized hollow-structural carbon spheres and showed that the carbon spheres worked like a "reservoir" to encapsulate sulfur into their hollows. Since carbon is electronically conductive, the reactions of sulfur can be completed inside the hollows of carbon spheres. Therefore, a sulfur−carbon composite made of carbon spheres exhibited outstanding electrochemical performance at both low and high current densities. They reported that the as-prepared composite displayed an initial specific capacity of 1071 mAh g^{-1} and maintained a capacity of 974 mAh g^{-1} at 0.5C after 100 cycles when it was coated into a cathode with a total sulfur content of 64.8% (i.e., 92.5% of the composite consisting of 70% sulfur and 30% carbon spheres).

The most impressive improvement by the sulfur−carbon composite approach has been reported by Xin et al. who claimed that the metastable small sulfur molecules (S_n with $n = 2-4$) could be confined in the carbon's micropores having a pore size less than the diameter of an S_8 ring [41]. A composite made of these small sulfur molecules exhibited an initial specific capacity of 1670 mAh g^{-1} (theoretically 1675 mAh g^{-1}), and still remained at 1149 mAh g^{-1} after 200 cycles with a single discharge voltage plateau at ∼1.9 V. More interestingly, the composite worked well with a $LiPF_6$−carbonate (a 1:1 mixture of ethylene carbonate and dimethyl carbonate by weight) electrolyte, which has been known to be chemically incompatible with PS [13]. As stated in Section 2.1, the molecular S_n allotropes with $n < 5$ are only present in the gas phase above 720 °C, and they spontaneously revert into the solid S_8 once the temperature cools down to room temperature [3,4]. Therefore, we are inclined to think that the excellent cycling performance is due to very low S/C ratio in the cathode. It was shown that the sulfur cathode contained a low sulfur content of 32% (i.e., composed of 80% sulfur−carbon composite that contains ∼40% sulfur) and a low sulfur loading of 1 mg cm^{-2}. In this case, the distance for the formed PS diffusing out of the cathode was so long that it was directly reduced to Li_2S before it could diffuse out of the cathode. The similar phenomenon also can be observed from the fast discharging. The single voltage plateau is due to the direct reduction from the solid and/or the dissolved S_8 into the solid Li_2S without passing through the dissolved PS intermediates, or in another word, the life of PS intermediates was too short to exhibit a discharge voltage plateau. In comparison with the PS species in solution, the solid sulfur and Li_2S have a much lower reactivity. This could explain why $LiPF_6$−carbonate electrolyte worked well in Xin et al.' case.

4.1.2. Metal oxide

Metal oxides are among the early materials used for trapping the dissolved PS in the cathode, which include electrochemically inactive metal oxides Al_2O_3 and SiO_2, as well as electrochemically active V_2O_5. To demonstrate this, Gorkovenko et al. [42] directly mixed these materials into sulfur cathodes and showed that the

cells with the addition of metal oxide had better capacity retention. The adsorption/absorption capacity and ability (strength) of the metal oxides to PS species are affected by the porosity, specific surface area, and the chemical affinity between PS species and metal atom in the metal oxide. This concept has been extended by modifying the pore's structure of the absorbents based on metal oxides of Al_2O_3 [43], SiO_2 [44], TiO_2 [45], and $Mg_{0.6}Ni_{0.4}O$ [46]. Recently, Evers et al. [45] studied the effect of pore parameters on the adsorption and absorption, and concluded that the PS species were preferentially absorbed within the pores of metal oxide, instead of being adsorbed on the surfaces of the particles. They showed that by optimizing the pore size of TiO_2, a cathode with 3.6 wt.% TiO_2 additive had a 37% higher specific capacity after 100 cycles than the cells without the additive.

4.1.3. Conducting polymer

Conducting polymers such as polyaniline (PAN) [47,48], polypyrrole (PPY) [49–52], and polythiophene (PT) [53,54] have been used to prepare sulfur−polymer composites. These polymers usually are proton-doped so that the protons can act as a bridge to link the polymer and PS anions via H-bonds. Furthermore, the conducting polymers themselves are electrochemically active, so they could provide some capacity. Therefore, the sulfur-conducting polymer composites more or less improved the cycling performance of Li/S cells.

It should be pointed out that all the materials above are based on the physical absorption and weak chemical adsorption, and that such absorption and adsorption are not very strong. To trap PS effectively, a large amount of adsorbents should be mixed into the cathode. Without exception, all approaches by the above materials fall into "two lows", i.e., low sulfur content and low sulfur loading. We have seldom seen that by these approaches, the sulfur content was greater than 70% by weight and the sulfur loading higher than 2 mg cm^{-2}. In addition, the PS anions carry two negative charges, and hence their electrical drag (transport) is inevitable in the process of cell's discharge and charge. Therefore, the implication of these approaches seems to be more academic than practical.

4.2. Protection of lithium anode

Protection of Li anode is the best choice for preventing redox shuttle, reducing gassing (swelling), and increasing the safety of Li/S cells. In order to protect Li effectively, the material of the protective layer should meet these criteria: (1) it is insoluble in the liquid electrolyte, (2) it is chemically stable against PS and Li metal, and (3) it should be highly Li^+ ionic conductive. Due to the extremely high reactivity of PS and Li metal, the selection of materials is very limited. Most of the known Li^+ ionic solid state electrolytes either react with Li metal or complex with PS to form soluble products. The few available publications on this subject are summarized as follows.

4.2.1. Physical barrier layer

Kim et al. [55] claimed that use of a separator made of fluorinated polymers with F/C < 2 assisted forming a LiF passivation layer on the surface of Li anode through a limited reaction between the Li metal and polymer. This approach has proven to improve the cycling efficiency and morphology of Li metal although the concern with the chemical stability of fluorinated polymers against PS still remains. Another Kim et al. [56] suggested that organosulfur compounds could complex with Li metal to form a protective layer. Based on this proposal, they coated a mixture of 2,5-dimercapto-1,3,4-thiadiazole and sulfonated polyaniline onto the surface of a Li anode by using a PEO binder, and made improvement in the capacity retention of the Li/S cells.

4.2.2. Gel polymer electrolyte

As stated in Section 3.3, the rough and loose deposition of Li metal is the major problem of the Li anode in the Li/S cells. The gel polymer electrolyte is able to stick the separator and Li anode together, which helps improve the morphology of Li plating. To demonstrate this, Mikhaylik et al. [14] placed a PEO–ceramic gel electrolyte layer between the separator and Li anode, finding that the resulting Li/S cells had significantly better capacity retention and lifted the thermal runaway temperature by at least 50 °C due to the compact deposition of the Li metal. A crosslinked gel polymer electrolyte layer has also been coated onto the Li surface by the in-situ polymerization of a solution consisting of a curable oligo(-ethylene glycol) dimethacrylate monomer, a photoinitiator, and a liquid electrolyte using UV curing method [57]. This approach led to an improved morphology of the Li plating in the Li/S cell.

4.2.3. Lithium alloy

Li alloy has been proposed to reduce the redox shuttle by Nimon et al. [58]. To do this, they made a Li–Al alloy by laminating a thin Al foil with a Li anode. Since Li–Al alloy forms a better Al_2S_3 protective layer, the Li/S cell using a Li–Al anode showed better specific capacity and capacity retention. A similar concept was demonstrated by Zheng et al. [59] who sputtered a thin platinum (Pt) layer onto the Li surface using the magnetron sputtering method. Since Pt forms an alloy with Li and it has stronger complexation ability with PS (being similar in manner to poisoning of a Pt catalyst by the sulfur species), a Li/S cell with the protected Li anode showed a specific capacity of 750 mAh g^{-1} after 90 cycles.

4.2.4. Pre-passivation of lithium

Another approach is the treatment of the Li anode using a reactive chemical to form a stable passivation layer before the Li/S cell is assembled [60]. Both oxidative compounds such as SO_2, SO_2Cl_2, and $SOCl_2$, and inorganic acids such as H_3PO_3 and H_3PO_4 have been proposed to form the insoluble and stable protective layer with Li metal. A Li/S cell with the treated Li showed higher discharge capacity as compared with the baseline cells.

4.3. Electrolyte additive

Many electrolyte additives have been studied for improving the Li/S cell's performance. The functions of additives include: (1) protecting Li anode, (2) enhancing the solubility and stability of PS in the liquid electrolyte, and (3) reducing the viscosity of the liquid electrolyte.

At low concentration, PS has been proven to be a very good additive for the formation of a stable Li_2S protective layer on the Li surface [61]. In the Li/S cells, however, the formed Li_2S will be chemically dissolved near the end of charge by the high-order PS, as suggested by Eq. (6). Therefore, a more effective additive is required for the protection of Li anode in the Li/S cells. The most important finding on this subject was, made by Mikhaylik et al. in 2008 [62], that $LiNO_3$ and its like compounds are exceptionally effective in inhibiting the PS redox shuttle. Surface analyses have shown that the oxidative $LiNO_3$ enables the Li metal to form a very favorable surface layer [63,64]. A storage test at 50 °C by our laboratory revealed that the surface layer formed in the presence of $LiNO_3$ was much more stable in a 0.5 m Li_2S_9 solution than that formed without $LiNO_3$ [65]. With the protection by such surface layers, the redox shuttle reactions (Eqs. (8) and (9)) are effectively suppressed so that the Li/S cell can be easily charged to the pre-set cutoff voltage, as shown by Cell 2 in Fig. 3, resulting in an over 99% coulombic efficiency. On the other hand, we found that $LiNO_3$ was reduced on the cathode below 1.5 V, and that the formed products severely affected the reversibility of sulfur cathode. To avoid this adverse effect, we suggested that the discharge voltage for Li/S cells with $LiNO_3$ as the additive or co-salt

should not be lower than 1.7 V [65,66]. In recent years, $LiNO_3$ has been widely used as the additive or co-salt for the electrolyte of the Li/S cells by many research groups [56,65–71]. However, the problems still remain, including that (1) it is gradually consumed on the Li anode, which leads to a decrease in the protection efficiency, and (2) it is a strong oxidative agent, which could cause a safety issue when a high concentration is used, especially at high temperature.

P_2S_5 was reported to promote the dissolution of PS and protect the Li anode, which led to an increase in the capacity retention of the Li/S cells [72]. In the Li/S cell, P_2S_5 plays two roles: (1) on the cathode it promotes the dissolution of PS into liquid electrolyte to enhance the cell's performance, and (2) on the Li anode it combines with Li_2S to form a P_2S_5–xLi_2S complex, which is a well-known highly Li$^+$-ionic conductive glass. Although the P_2S_5–xLi_2S complex is soluble in the liquid electrolyte, a 3–5 μm thick solid P_2S_5–xLi_2S layer still was detected on the Li surface. This solid-state electrolyte layer protected Li, and as a result the Li/S cells having P_2S_5 additive exhibited a reversible capacity of 900–1350 mAh g^{-1} with coulombic efficiencies higher than 90% for over 40 cycles.

Liang et al. [73] proposed that the "dead" Li_2S and Li_2S_2 deposited on the Li surface could be recovered to active (soluble) PS by employing a 0.05–0.5 M LiBr as the additive or co-salt of the liquid electrolyte. By charging Li/S cell to 3.5 V, the Br$^-$ anions were oxidized to bromine (Br$_2$), which immediately oxidized the insoluble Li_2S and Li_2S_2 into a soluble (active) polysulfide bromide compound (Br–S$_n$–Br). Results turned out that LiBr added small amount of capacity above 2.3 V, and meanwhile caused severe corrosion of the cathode current collector (stainless steel) due to the high charging cutoff voltage (3.5 V). They contributed the added capacity to the reduction of the formed polysulfide bromide compound, and agreed that the LiBr was a part of the cathode active materials in the form of polysulfide bromide compounds.

Based on HSAB (hard and soft acids and bases) theory, the Li$^+$ ion is a hard acid and the PS anion is a soft base. Their combination (i.e., the PS compounds) is not stable. In solution, PS molecules tend to disproportionate as suggested by Eq. (7). The addition of a soft acid into the electrolyte solution is expected to stabilize PS molecules. This concept has been confirmed by adding ionic liquid as the electrolyte additive for Li/S cells. Many researchers have shown that the addition of ionic liquids tends to enhance the specific capacity and stabilize the capacity retention [74–76]. A similar phenomenon has also been reported on Li/air cells, in which addition of a quaternary ammonium or an ionic liquid into the liquid electrolyte increases the cell's capacity and reversibility because the added ammonium cations (a soft acid) stabilize superoxide and peroxide anions (O_2^- and O_2^{2-}, both are a soft base) and meanwhile increase their solubility in the liquid electrolytes [77,78].

With the dissolution of PS, the viscosity of the electrolyte solution is dramatically increased, which greatly reduces the Li/S cell's power capability, especially for the operations at low temperature or/and at high current rate. This problem gets more severe for the electrolytes consisting of solvents with high boiling points. To alleviate this problem, Choi et al. [79] investigated the effect of toluene on the Li/S cell's performance by using a 1 M LiCF$_3$SO$_3$ in tetra(ethylene glycol) dimethyl ether electrolyte. They found that addition of toluene increased the cell's capacity due to a reduction in the solution's viscosity. For example, when a 5% of toluene was added into the liquid electrolyte, the Li/S cell displayed an initial specific capacity of 750 mAh g^{-1}, which was 1.8 times higher than the cell without toluene.

4.4. Inswellable binder

In response to the large porosity change accompanied with the discharge and charge processes of sulfur cathode, the author first

proposed an inswellable binder for the sulfur cathode based on a polyelectrolyte, poly(acrylamide-co-diallyldimethylammonium chloride) (AMAC), with the chemical structure below [80]:
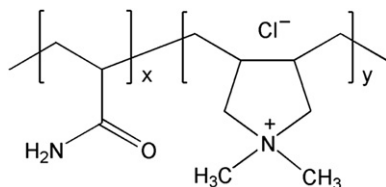
This polymer is highly soluble in water while not swelling in the organic electrolytes. Therefore, the porous structure of the cathode with AMAC binder is not affected by the dissolution of PS and re-deposition of Li_2S_2 and Li_2S. Results showed that the cathode with AMAC binder had much better capacity retention than those using PEO binder. Unfortunately, the AMAC binder caused severe pitting corrosion of the Al substrate during the slurry-coating process. This is because the AMAC aqueous solution dissociates Cl^- anions, which form galvanic cells between sulfur particles and Al substrate. To solve the problem of Al corrosion, we developed a two-step procedure for the slurry coating of sulfur cathode [12], which consists of the first step making a sulfur–AMAC composite using an aqueous slurry and the second step coating the composite onto the Al substrate using another binder and an organic solvent. By this new procedure, we showed that a high sulfur-loading cathode (containing 72% sulfur in a sulfur-loading of 3 mg cm^{-2}) retained a specific capacity of 568 mAh g^{-1} after 107 cycles at 0.5 mA cm^{-2}.

Other inswellable binders reported so far include gelatin [81–83], sodium carboxymethyl cellulose (CMC) [84], Nafion [84], polyacrylic acid (PAA) [85], and the blend of CMC and styrene butadiene rubber (SBR) [86,87]. A common characteristic of these binders is that they are water-soluble while being insoluble in the organic liquid electrolytes. Attributed to the stabilized porous structure of the sulfur cathode, all these binders have been reported to provide better performance in terms of the specific capacity and capacity retention of sulfur. On the other hand, the insoluble property reduces the chemical reactivity of the binders with PS solution. For example, SBR rubber could be stable in PS solution although it contains reactive >C=C< unsaturated bonds.

4.5. New concepts

4.5.1. Binder-free sulfur cathode

For high sulfur-loading cathode, a binder-free electrode can be easily prepared by using the melt method since in this case sulfur itself can serve as the binder. To demonstrate this technique, Xu et al. [88] cast a cathode slurry consisting of 85% sulfur and 15% carbon dispersed in isopropanol onto a carbon-coated Al foil, followed by heating the foil at 150 °C for 45 s. Cooling down to room temperature resulted in a well-coated sulfur cathode, and the result showed that in spite of the high sulfur loading, the binder-free cathode had the same or even better cycling performance as compared with the cathodes using the conventional PEO binder.

Another technique for the binder-free sulfur cathode was reported by Elazari et al. [89] who used a carbon cloth as the current collector and had sulfur impregnating into the pores of the carbon fibers. To make an electrode, the fine sulfur powder was first dispersed onto the carbon cloth, and then impregnated into the carbon' pores by heating at ∼155 °C for 10–15 h. The purpose for the long heating time was to ensure that the sulfur melt effectively diffused into the tiny pores of carbon fibers. Due to the excellent distribution of sulfur in carbon's pores, a cathode having a sulfur loading of 6.5 mg cm^{-2} was shown to retain a specific capacity of

over 800 mAh g^{-1} after 80 cycles. A similar procedure was followed by Hagen et al. [90] with a few differences in the carbon substrate and heating time. Hagen et al. started with a nonwoven carbon gas diffusion layer, deposited a nanotube carbon layer using the chemical vapor deposition (CVD) method, and then homogeneously dispersed sulfur powder on the nanotube carbon layer, followed by heating at 150 °C for 1–2 min. An extreme example of this method showed that a cathode with a sulfur loading up to 20 mg cm^{-2} still exhibited a specific capacity of ∼900 mAh g^{-1} at 0.64 mA cm^{-2}. It is interesting to note that the initial specific capacities of sulfur by Elazari et al. [89] and Hagen et al. [90], respectively, were very close to each other, indicating very little effect of the heating time on the discharge performance of the sulfur–carbon composites. This fact again indicates that the initial mixing status of sulfur and carbon in the sulfur cathodes is not important for the performance of Li/S cells.

4.5.2. Dual-layer structural cathode

In our laboratory, we first proposed a dual-layer structural cathode for the reduction of self-discharge of the primary Li/S cells [91]. Due to the slight solubility of elemental sulfur in organic liquid electrolytes, a Li/S cell suffers from much faster self-discharge rate than other primary lithium cells such as Li/MnO_2 and Li/SO_2 batteries. To solve this problem, we intentionally separated the sulfur and conductive carbon by making a dual-layer structural cathode, where a porous pure sulfur layer was sandwiched between the Al current collector and a porous carbon layer. Thus, the porous carbon layer plays two roles: (1) it absorbs the dissolved sulfur during new cell's storage, and (2) it absorbs the dissolved PS and meanwhile serves as the reaction sites for the reduction of the dissolved PS. In this way, we showed that the Li/S cells had a much longer shelf-life and exhibited similar specific capacity as compared with those employing the conventional sulfur cathode prepared by mixing sulfur and carbon together in the same content and loading of sulfur. In addition to the primary battery, we also extended the dual-layer structural cathode to the rechargeable Li/S batteries with different cathode configurations [91]. Operation of the above batteries is attributed to the high solubility of sulfur and PS in the liquid electrolytes. On discharge, sulfur is first reduced on the surface of Al substrate into Li_2S_8, which dissolves into the liquid electrolyte, followed by migrating to the porous carbon layer (driven partially by the effect of electric transport) and absorbing into the pores of carbon layer. With the reduction and dissolution of the sulfur layer, the conductive carbon layer and Al substrate eventually get contact with each other, and at this point the carbon layer acts as the reaction sites for further reduction of the dissolved PS.

The same concept was reported independently by Su et al. who referred to the porous carbon layer as the "interlayer" [92]. As an example, they placed a MWCNT (Multi-Walled Carbon Nanotube) paper as the "interlayer" between the separator and the regular sulfur electrode. They found that the Li/S cell having such a conductive interlayer exhibited outstanding cyclability with a specific capacity of >800 mAh g^{-1} over 100 cycles, and attributed the excellent performance to the fact that the interlayer works as not only an "upper current collector" to improve the active material utilization but also a "polysulfide stockroom" to maintain the cycle stability and good system efficiency.

It should be noted that when speaking of the energy density of a Li/S cell, one must consider the total mass of the conductive carbon in the cathode no matter what the electrode's configuration is. By taking the mass of the second carbon layer into account, we admit that the improved cyclability of the Li/S cells was made at the expense of energy density, being the same problem as met in the sulfur–carbon composite approach.

4.5.3. Li/S liquid cell

A Li/S liquid cell, or called a Li/dissolved sulfur cell, was among the earliest approaches in the study of Li/S batteries. In early time, the interest was in the primary battery with focus on the Li/S cell's energy density, power density, and shelf life by exploring electrolyte solvents with high PS solubility and low viscosity [93–96]. A small difference between the Li/S liquid cell and the conventional Li/S cell is the voltage profile of the first discharge, as indicated in Fig. 4, where the dissolved Li_2S_9 was used as the liquid cathode. Since there is no free sulfur in the Li_2S_9 solution, the first discharge of the liquid cell does not show the upper voltage plateau near 2.3 V, whereas that of the conventional Li/S cell displays a clear voltage plateau at ∼2.3 V as indicated by the arrow in Fig. 4a. In the fifth cycle, both cells suffered from a strong redox shuttle so that their voltage could not be charged above 2.5 V. The attempt to recharge the Li/S liquid cells was not very successful because of the redox shuttle and corrosion of the dissolved PS to the Li anode [97,98]. However, the $LiNO_3$ additive made it possible for the liquid cells to cycle better than the conventional Li/S cells [11]. In these cells, the positive electrode is a porous carbon layer coated onto an Al substrate with the Li_2S_9 active cathode material dissolved in the liquid electrolyte. Since the Li anode was protected by $LiNO_3$ additive, the cell started with a specific capacity of 556 mAh g^{-1} having a coulombic efficiency of 98.6% and remained 520 mAh g^{-1} after 70 cycles, which outperformed the conventional Li/S cell having a similar sulfur loading. Although our original purpose of that work was to stress the importance of PS dissolution in the Li/S cell's cycling performance, the improved performance of the Li/S liquid cells has revealed that use of a PS-dissolved electrolyte in conventional Li/S cells must benefit to the cells' energy density and cyclability.

It should be pointed out that the cycling performances of Li/S cells are greatly affected by the concentration of PS solution due to the disproportionation of PS in the electrolyte solutions. As indicated by Eq. (7), the disproportionation of PS produces low soluble elemental sulfur and low-order PS, which become inactive once they are deposited out of the electrolyte solution or into the pores of the microporous separator. Therefore, in the Li/S cells the disproportionation of PS should be minimized for high specific capacity. To verify this, we studied the effect of electrolyte/sulfur (E/S) ratio on the cyclability of Li/S cells, finding that the optimized E/S ratio is the minimum value which allows the dissolved PS to diffuse out of the cathode without resistance [99]. This value can be empirically determined by gradually reducing the E/S ratio until a voltage delay starts to appear in the beginning of the first discharge of Li/S cells [99].

4.5.4. Li-free Li/S cell

Li metal has long been known to be an important factor to affect the safety of Li/S cells. For a charged Li/S cell, its thermal runway at elevated temperature mainly arises from the chemical reaction of Li metal with the dissolved PS, and its inducing reactions with the electrolyte solvents and oxygen/nitrogen from air. Therefore, replacing the Li anode is no doubt the most effective approach for increasing the safety of Li/S cells. In this effort, it has been proposed to use Li_2S as the starting cathode material, and tin [100–103] or silicon [103–106] as the anode material. In the initial charge period of such cells, the Li_2S is oxidized through a series of PS intermediates to sulfur or dissolved high-order PS on the cathode, whereas Li$^+$ ions are reduced to form Li–Sn or Li–Si alloy on the anode. Since only equal equivalents of Li alloys as the sulfur and PS in the cathode can be formed on the anode, the safety of Li/S cell is assumed to be improved significantly.

In order to demonstrate the principle of Li_2S as the starting active cathode material, Fig. 5 shows the charge and discharge voltage curves for the selected cycles of a Li/Li_2S half-cell. It is shown that in the first charge, the Li/Li_2S cell suffers from very high polarization. In particular, there is a significant voltage peak in the very beginning of charge, which is believed to be formed for the same reason of peak 2 in Fig. 1. Since the starting Li_2S is neither electrically conductive nor soluble in the liquid electrolyte, its
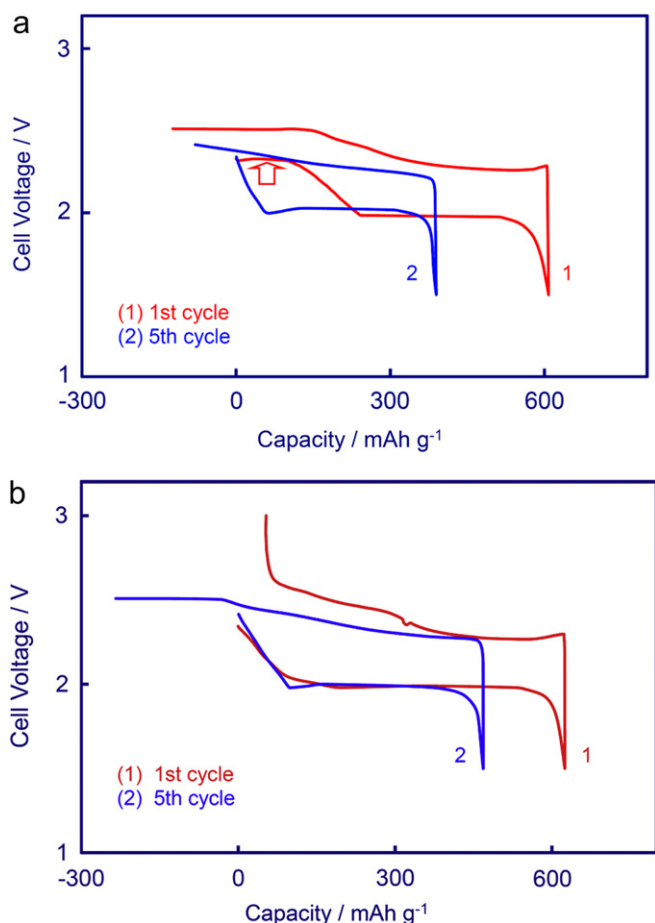

Fig. 4. Discharge and charge voltage curves of the first and fifth cycles. (a) Conventional Li/S cell, (b) Li/Li_2S_9 liquid cell. Reproduced from Ref. [11] with permission of Elsevier.
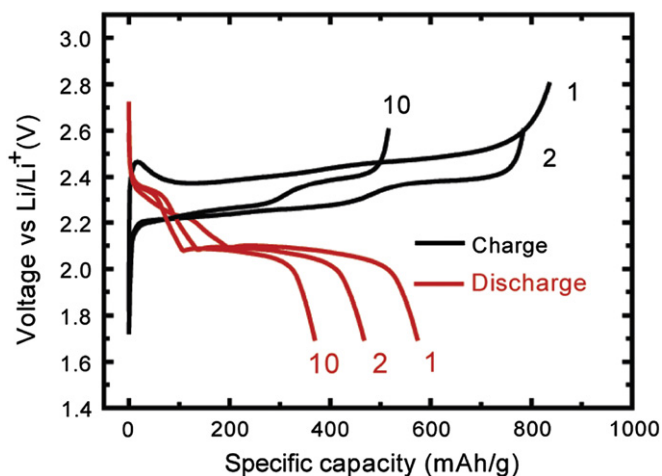

Fig. 5. Charge and discharge voltage curves for selected cycles of a Li/Li_2S half-cell, in which the specific capacity is referred to the mass of Li_2S at a C/8 (146 mA g^{-1}) current rate. Reproduced from Ref. [103] with permission of America Chemical Society.

oxidization experiences very high polarization. With electro-chemical oxidization and/or the recombination by high-order PS (as shown by Eq. (6)), the insoluble Li_2S is converted into the soluble PS, which hence dissolves into the liquid electrolyte and reduces the cell's polarization. Once the PS dissolves into the liquid electrolyte, the Li/Li_2S cell can operate as a regular Li/S cell where the electrochemical reactions occur on the surface of the conductive carbon. The initial polarization of Li_2S oxidation has been observed much more severely from the cyclic voltammetric tests, which show Li_2S cannot be oxidized until 3.5 V in the first positive potential scanning [100,102]. A drawback of the Sn/Li_2S and Si/Li_2S cells is that they cannot withstand over-discharge. The insoluble SnS_n and SiS_n could be formed and permanently deposited on the surface of the lithium alloy once the cell is over-discharged to low voltages.

5. Concluding remarks

As reviewed above, significant advancements in the liquid electrolyte Li/S cells have been made in recent years, however, challenges still remain. Fundamentally, the dissolution of elemental sulfur and PS in the organic liquid electrolytes is inevitable, and it is essential for the operation of Li/S cells. Since sulfur and PS are neither electronically conductive nor ionically conductive, their redox only can take place on the surface of the conductive carbon (exactly the electrolyte–carbon interface). Therefore, the Li/S cell is really a liquid electrochemical cell. On the other hand, polysulfide anions carry two negative charges, their electric drag (transport) between two electrodes must be present as long as the Li/S cell runs. Sulfur–carbon composites have proven to be effective in suppressing the diffusion of the dissolved PS out of the cathode. However, such improvements are made at expense of the energy density due to the introduction of extra electrochemically inactive carbon. Even using these composites containing a large amount of carbon, the Li/S cell still is a liquid cell with the small difference that the dissolved PS are adsorbed or absorbed in the surfaces and pores of the carbon. Keeping the effect of PS's electrical drag (transport) in mind, we believe that the most effective approach for improving the cyclability and safety of Li/S cells is the protection of the Li anode against the redox shuttle and corrosion of the dissolved PS. The liquid electrolyte plays an important role in dissolving PS and determining the cell's power capability. An electrolyte additive provides a facile way for suppressing the PS redox shuttle and improving the morphology of the Li deposition. A $LiNO_3$ additive solves the low coulombic efficiency problem of Li cycling, however, it is gradually consumed on both the cathode and Li anode, and its strongly oxidative property could cause a safety issue. More effective and safer additives are needed for advancing Li/S technology. Since PS and polysulfide anionic radicals are extremely reactive, high priority should be placed on the chemical compatibility for the selection of the cell's materials including electrolyte solvent, salt, and cathode's binder. No matter what approaches are taken, the cathode must have a reasonably high content and loading of sulfur to retain the advantage of the high energy density of Li/S cells.

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